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1 **A first report of rare earth elements in Northwestern Mediterranean seaweeds**

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10

11 **Abstract**

12 The concentrations of rare earth elements (REE) were determined by ICP-MS in dominant seaweed
13 species, collected from three locations of the northwestern Mediterranean Sea. This is the first study
14 to define levels and patterns of REE in macro algae from these coastal areas.

15 Rare elements are becoming emerging inorganic contaminants in marine ecosystems, due to their
16 worldwide increasing applications in industry, technology, medicine and agriculture.

17 Significant inter-site and interspecies differences were registered, with higher levels of REE in
18 brown and green macro algae than in red seaweeds. Levels of light REE were also observed to be
19 greater compared to heavy REE in all samples.

20 One of the investigated locations (Bergeggi, SV) had higher REE and Σ REE concentrations,
21 probably due to its proximity to an important commercial and touristic harbor, while the other two
22 sites were less affected by anthropogenic contaminations, and showed comparable REE patterns
23 and lower concentrations.

24

25 **Capsule:** rare earth elements in seaweeds

26

27 **Keywords:** REE, seaweeds, Mediterranean Sea, pollution tracers.

28

1. Introduction

Rare earth elements (REE) are a group of chemical elements including yttrium (Y), scandium (Sc) and lanthanides (from lanthanum to lutetium). Despite their name, REE are not that rare in the natural environment, being the fifteenth most abundant component of the earth's crust (USEPA, 2012). REE are further subdivided into light REE (LREE), including lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd) and samarium (Sm); and heavy REE (HREE), including gadolinium (Gd), europium (Eu), terbium (Tb), dysprosium (Dy), thulium (Tm), ytterbium (Yb), holmium (Ho), erbium (Er), lutetium (Lu) and yttrium (Y) (Anastopoulos et al., 2016).

REE mainly enter into oceans through atmospheric fallout (De Baar et al., 1983) and fluvial inputs (Frost et al., 1986), and have been frequently investigated as natural tracers of biogeochemical processes (Oliveri et al., 2010). As the distribution patterns of REE in the water column are already known, it is possible to utilize these patterns for tracing water masses or to identify pollution sources in seawater (Censi et al., 2004).

In fact, in the last decade, the worldwide use of REE in industrial applications (electronics, nuclear energy, metallurgy, medicine, computer manufacturing) and in some countries (such as China) for use in fertilizer and feed additives, has increased levels of REE in water environments (Mashitah et al., 2012; Hermann et al., 2016). Thus, REE can be considered as emerging contaminants and pose a potential risk for marine and freshwater ecosystems.

The Mediterranean Sea is a semi-enclosed sea; concentrations of trace elements and REE in this basin are higher than those registered in other nutrient-depleted surficial waters (Greaves et al., 1994; Strady et al., 2015). Numerous investigations regarding patterns of dissolved and particulate REE have been performed in this basin (e.g. Censi et al., 2004; Martinez-Boti et al., 2009; Tranchida et al., 2011; Roussiez et al., 2013; Ayache et al., 2016); conversely, occurrence and distribution of REE in marine biota have scarcely been investigated. To our knowledge, there are only two studies that have analyzed the distribution of REE in plankton from the Mediterranean Sea

56 (Strady et al., 2015; Battuello et al., 2017); examining REE in marine organisms is of great
57 importance because of their increasing levels in seawater environments and, consequently, in the
58 marine food chain.

59 Of the marine organisms that can be utilized as bioindicators of trace elements and REE in marine
60 environments, seaweeds have several advantages as they are widespread, easy to collect and have a
61 considerable ability to take-up trace elements in solution and concentrate them. Moreover, as they
62 are at the base of the marine food chain, macro algae are essential in the transfer of trace elements
63 to higher trophic levels.

64 We determined REE concentrations and distributions in seaweeds from three different sites located
65 in Northwestern Mediterranean coastal areas. These sites have different environmental protection in
66 the Ligurian and Northern Tyrrhenian Sea. The macro algae species collected for this study were
67 the most abundant and widespread in all three sampling sites and were represented by the three
68 phylum Chlorophyta (green algae), Ochrophyta (brown algae) and Rodophyta.

69 Macro algae species from these three locations were the subject of a previous investigation that
70 focused on essential and nonessential trace elements, in the perspective of identifying the species
71 potentially suitable for human and animal nutrition, as well to identify any potential risks for
72 consumers due to the presence of toxic metals such as lead, cadmium and mercury in seaweeds of
73 Mediterranean origin (Squadroni et al., under review).

74 In this study, we aimed to measure, for the first time, the concentrations of REE in marine
75 Mediterranean seaweeds, identifying patterns and fractionations of REE, and verifying the potential
76 use of REE as pollution tracers in the studied area.

77

78 **2. Materials and methods**

79 *2.1. Sampling area*

80 All three sampling locations were situated in the northwestern Mediterranean Sea (Figure 1).

81 The first sampling site was located in Bergeggi (SV), a Marine Protected Area of the Ligurian Sea
82 (44°14'26. 94"N, 8°26'50. 98"E, General Reserve named B zone.) Here, human activities are
83 restricted and regulated by the Italian law. Close to this site is located the industrial and commercial
84 harbor of Vado Ligure (SV), characterized by high shipping traffic.

85 The second site was in the Island of Elba (Tyrrhenian Sea, 42°42'35. 17"N, 10°24'44. 97"E), five
86 nautical miles off the Tuscan coast. Elba is the most populated island of the Tuscan archipelago,
87 especially in summer.

88 The third sampling site was located in the little Capraia Island, (43°4'26. 90"N, 9°49'39.63"E, in the
89 National Park of the Tuscan Archipelago, PNAT), another Marine Protected Area of the Ligurian
90 Sea, about 30 nautical miles off Tuscan coast. The island has few inhabitants and no industrial
91 activities.

92 Seaweed samples were collected in summer 2016. After collection, the macro algae were washed on
93 board with seawater and then stored in refrigerated conditions. The specimens were transported to
94 the laboratory and examined under the stereomicroscope, after being cut into thin sections, in order
95 to identify the macro algae species. Before analyzing the seaweeds for REE content in the chemical
96 laboratory, samples were rinsed with tap water, followed by a rinse with distilled water, then freeze-
97 dried and homogenized to obtain a fine powder. Approximately 1-1.5 g of each sample were
98 utilized for quantitation of REEs.

99 *2.2 Determination of REE*

100 Samples mineralization was performed using a microwave digestion lab station (Ethos 1, Milestone,
101 Shelton, CT, USA), equipped with a 10 positions rotor for high pressures polytetrafluoroethylene
102 (PTFE) digestion tubes.

103 All digestion tubes were cleaned with concentrated acid, rinsed with ultrapure water and dried at
104 room temperature under a chemical hood. Disposable polypropylene tubes were used to storage
105 mineralized samples. Freeze-dried samples (1.0-1.5 g) were directly weighed into PTFE digestion

tubes. 7 mL of HNO₃ (70% v/v) and 1.5 mL of H₂O₂ (30% v/v) were then added before the microwave digestion process, programmed as follows: heating to 130°C in 8 min, hold for 2 min, heating to 200°C in 8 min, hold for 5 min; cooling for 30 min. Digested samples were then quantitatively transferred to 50 mL polypropylene tubes and gravimetrically diluted to a final weight of 50 g with ultrapure water.

REE determination was performed by Inductively Coupled Plasma-Mass Spectrometer (ICP-MS Xseries II, Thermo Scientific, Bremen, Germany) equipped with a multi-vial auto sampler (ASX 520, CETAC Technologies, Omaha, NE, USA). Instrument was tuned daily before each analytical trial. Certified Reference Materials (REE-1 from the National Institute of Standard and Technology), blank reagents and standard solutions were processed during each analytical session to verify performances of the methods. The limit of quantification (LOQ) was 0.010 mg Kg⁻¹. Results were expressed in mg Kg⁻¹ dry weight as the mean for each site with standard deviation; the sum of REE (Σ REE), of light REE (LREE) and of heavy REE (HREE) are also shown (Table 1).

2.3 Statistical analysis

The one-way analysis of variance (ANOVA) was employed to compare the average contents of the sum of REE (Σ REE) in macro algae between the three sampling sites and between the macro algae species in the same site (Table 2). The unpaired t-test was used to compare the average contents of Σ REE in macro algae between sites 2 and 3. Results were considered statistically significant at p values of < 0.05. Graph Pad Statistics Software Version 6.0 (GraphPad Software, Inc., USA) was used for statistical evaluations.

3. Results and Discussion

REE are typical lithophile elements, with scarce presence in biological tissues. Seaweeds mostly develop in marine environments in contact with sediments and suspended particulate from geologic origin is present in their environment. Therefore, fine geological particulate, containing REE, are incorporated in plants tissues in different amounts.

131 The concentrations of REE in marine macro algae from the three collection sites of the
132 Northwestern Mediterranean Sea are shown in Table 1 (mg Kg^{-1} dry weight). REE and ΣREE are
133 also graphically presented for the three sites (Figure 2) and for the analyzed seaweeds (Figures 3
134 and 4), to facilitate comparison.

135 A high variability in REE concentrations between the three sampling sites and between species was
136 recorded; the REE concentrations, however, consistently followed the same trend, and
137 concentrations of LREE were always higher than HREE.

138 3.1 Inter-site variability

139 In Figures 2a and 2b, mean REE levels in the three sampling sites are graphically represented. As
140 shown, the specific area of collection greatly affected REE concentrations. In fact, macro algae
141 from site 1 (Bergeggi, SV) had the highest concentrations for all the analyzed REE (Table 1). In site
142 1, the highest REE values were found in the Ocrophyta *Halopteris filicina* (Ce 8.8 mg Kg^{-1} , La 4.3
143 mg Kg^{-1} , Nd 4.1 mg Kg^{-1} , Y 3.4 mg Kg^{-1} , Sc 1.5 mg Kg^{-1} , Pr 1.1 mg Kg^{-1} , Sm and Gd 0.87 mg Kg^{-1} ,
144 1 , Dy 0.64 mg Kg^{-1} , Er 0.32 mg Kg^{-1} , Yb 0.27 mg Kg^{-1} , Tb and Ho 0.22 mg Kg^{-1} , Eu 0.17 mg Kg^{-1} ,
145 Tm 0.80 mg Kg^{-1} , Lu 0.78 mg Kg^{-1}) and the lowest concentrations were found in the Rodhopyta
146 *Ganonema farinosum* (Ce 4.8 mg Kg^{-1} , La 2.5 mg Kg^{-1} , Nd 2.2 mg Kg^{-1} , Y 2.0 mg Kg^{-1} , Sc 0.84 mg
147 Kg^{-1} , Pr 0.55 mg Kg^{-1} , Sm and Gd 0.46 mg Kg^{-1} , Dy 0.35 mg Kg^{-1} , Er 0.19 mg Kg^{-1} , Yb 0.15 mg
148 Kg^{-1} , Eu 0.10 mg Kg^{-1} , Tb and Ho 0.080 mg Kg^{-1} , Tm and Lu 0.030 mg Kg^{-1}).

149 Despite being located in a marine protected area, site 1 seems to be greatly affected by being
150 situated close to an important industrial and touristic harbor.

151 In site 2 (Elba Island, LI), we detected the highest levels of all elements in the Clorophyta *Flabellia*
152 *petiolata* (Ce 3.5 mg Kg^{-1} , Y 2.3 mg Kg^{-1} , La 2.2 mg Kg^{-1} , Nd 1.9 mg Kg^{-1} , Sc 0.66 mg Kg^{-1} , Pr
153 0.47 mg Kg^{-1} , Gd 0.45 mg Kg^{-1} , Sm 0.40 mg Kg^{-1} , Dy 0.34 mg Kg^{-1} , Er 0.18 mg Kg^{-1} , Yb 0.15 mg
154 Kg^{-1} , Eu and Ho 0.10 mg Kg^{-1} , Tb 0.091 mg Kg^{-1} , Tm 0.040 and Lu 0.033 mg Kg^{-1}).

155 In site 3 (Capraia Island, LI), the highest REE concentrations were found in the Ocrophyta
156 *Halopteris scoparia* (Ce 6.2 mg Kg^{-1} , La and Nd 2.7 mg Kg^{-1} , Y 1.9 mg Kg^{-1} , Sc 0.87 mg Kg^{-1} , Pr

157 0.65 mg Kg⁻¹, Sm and Gd 0.51 mg Kg⁻¹, Dy 0.34 mg Kg⁻¹, Er 0.17 mg Kg⁻¹, Yb 0.13 mg Kg⁻¹, Eu
158 0.10 mg Kg⁻¹, Ho 0.073 mg Kg⁻¹, Tb 0.070 mg Kg⁻¹, Tm 0.025 mg Kg⁻¹, Lu 0.022 mg Kg⁻¹) and the
159 lowest levels were found in the Rodhopyta *Dudresnaya verticillata*.

160 Sites 2 and 3 seem to be less affected by anthropogenic contamination, and REE mean values were
161 half of those registered in site 1.

162 In Table 2, the comparison between the ΣREE by one-way ANOVA showed a highly significant
163 difference in concentrations between the three locations ($p < 0.0001$). However, the comparison
164 between only sites 2 and 3 using the unpaired t-test resulted in a non-significant difference ($p >$
165 0.05), highlighting that site 1 showed very different levels of REE in seaweeds, while between sites
166 2 and 3, ΣREE values did not differ significantly.

167 3.2 Interspecies variability

168 The total levels of REE (ΣREE) are shown for each analyzed species in the three examined
169 locations (Figure 3).

170 In site 1, Bergeggi (SV), the highest values were found overall, especially in green and brown
171 macro algae, while in sites 2 and 3, REE values were lower; however, there was a high interspecies
172 variability in the same sampling site. In fact, in site 1 (Figure 3), the total REE content was in the
173 following decreasing order *Halopteris filicina* (ΣREE 27 mg Kg⁻¹ d.w.) > *Flabellia petiolata* >
174 *Padina pavonica* > *Codium bursa* > *Ganonema farinosum* (ΣREE 15 mg Kg⁻¹ d.w.); in site 2, the
175 order was *Flabellia petiolata* (ΣREE 15 mg Kg⁻¹ dry weight (d.w.) > *Dictyota dichotoma* > *Codium*
176 *bursa* = *Padina pavonica* > *Peyssonnelia squamaria* > *Laurencia obtusa* > *Caulerpa racemosa* >
177 *Halopteris filicina* (ΣREE 2.1 mg Kg⁻¹ d.w.); and finally, in site 3, the order was *Halopteris*
178 *scoparia* (ΣREE 17 mg Kg⁻¹ d.w.) > *Padina pavonica* > *Halimeda tuna* > *Peyssonnelia squamaria*
179 > *Cystoseira spp* > *Flabellia petiolata* > *Codium bursa* > *Dudresnaya verticillata* (ΣREE 2.3 mg
180 Kg⁻¹ d.w.). A comparison between the three species that were collected in all three locations (*F.*
181 *petiolata*, *C. bursa*, *P. pavonica*) is shown in Figure 4. The REE pattern was similar, but

182 concentrations differed in the same species in the two green macro algae *F. petiolata* and *C. bursa*
183 from the three sites; the brown macro alga *P. pavonica* showed almost the same levels of REE in
184 sites 2 and 3, but a higher value in site 1.

185 As shown in Table 2, the one-way interspecies comparison revealed highly significant differences
186 between the different macro algae species for each site. This finding is in line with the scarce
187 literature regarding REE in macro algae. In fact, other authors have underlined the interspecies
188 variability in REE levels. Fu and coauthors (2000) suggested that REE patterns are division-
189 dependent; while Sakamoto and coauthors (2008) indicated that the mechanism of uptake could be
190 different and related to seaweed morphology, even if the accumulation of REE in seaweed is still
191 not elucidated.

192 3.3 Chondrite-normalized REE pattern (Leedey Oklahoma chondrite)

193 To define a normalized REE pattern (Figure 5), we utilized the normalized values reported
194 by Masuda (1975) for the Leedey chondrite, which is considered the most primitive chondrite
195 (Sakamoto et al., 2008). Chondrite meteorites are, in fact, used as a reference for the normalization
196 of REE, as they are thought to be similar to the original composition of the Earth's crust (Masuda et
197 al., 1973). Moreover, during this meteorite formation, lanthanide fractionation did not occur (Song
198 et al., 2006; Antonina et al., 2013), therefore, if fractionation between REE in seaweeds occurred,
199 the comparison with the chondrite pattern could disclose this phenomenon.

200 In our study, the REE patterns were comparable in the three sites (Figure 5), even if, as previously
201 indicated, site 1 (Bergeggi, SV) showed higher overall REE concentrations than the other two
202 locations. The REE Ce and Eu have additional valences compared to the other lanthanides, and
203 when Ce and/or Eu concentrations are enriched or depleted compared to the levels recorded in
204 chondrite, this phenomenon is defined as a Ce or Eu (positive or negative) anomaly. In seaweeds
205 from the three sites, a Eu negative anomaly was observed (Figure 5), while the REE ratios (Ce/La,
206 Gd/Yb, La/Yb) were almost the same in the three different stations (mean values 1.8, 3.3 and 17,
207 respectively).

208 The Eu anomaly is thought to be strictly dependent on lithology (Moller et al., 2004) and
209 enrichment or depletion was explained by the Eu capacity to be mostly incorporated into
210 plagioclase minerals.

211 Despite the very different sites of origin, the chondrite-normalized pattern profile of Mediterranean
212 seaweeds appeared to be very similar to the pattern found by Mashitah and co-authors (2012) in
213 brown seaweeds from Malaysian coasts.

214 The REE patterns normalized by chondrite (Figure 5) are typical of geological materials
215 such as sediments, confirming that REE measurements are compatible with a geological material
216 incorporated in macro algae tissues in different amounts. Moreover, the patterns are similar among
217 sampling sites suggesting that correspond to sediments of similar origin.

218 3.4 Comparison with REE in biota

219 In a previous study, we analyzed Ce and La concentrations in marine zooplankton from the
220 Northwestern Mediterranean Sea (Battuello et al., 2017). We observed that concentrations for both
221 these elements decreased from herbivorous to carnivorous copepods, and were in the average range
222 of 0.50 - 1.86 mg Kg⁻¹ for Ce and 0.28 - 0.88 mg Kg⁻¹ d.w. for La (lowest values in carnivores).

223 In this investigation, Ce and La in seaweeds were in the medium range of 7.2 - 2.5 mg Kg⁻¹ and 3.7
224 - 1.3 mg Kg⁻¹ d.w., respectively, showing the higher ability of REE to accumulate in seaweeds
225 compared to zooplankton. As far as we know, we cannot compare these results with other seaweeds
226 from the Mediterranean Sea, but a few studies have been performed in other parts of the world. For
227 example, Hou and Yan (1998) analyzed La levels in Chinese coast seaweeds, finding the highest
228 values reported in seaweeds to date, 10.14 mg Kg⁻¹ d.w. in green macro algae and 6.73 mg Kg⁻¹ d.w.
229 in red macro algae, while the highest value we found for lanthanum was 4.3 mg Kg⁻¹ in *H. filicina*
230 and *P. pavonica* from site 1.

231 Masitah (2012) analyzed REE concentrations in *P. pavonica* (Malaysian coast), and found ΣREE
232 values ranging from 62 to 8.4 mg Kg⁻¹, higher concentrations than in the Mediterranean area, where

the range we registered was 22 - 7.9 mg Kg⁻¹ (Table 1, Figure 2). REE in *Padina sp.* from the Malaysia areas decreased in the following order: Ce>Nd>La>Pr>Gd>Sm>Dy>Er>Yb>Eu=Tb>Ho>Tm>Lu.

In our study, in site 1 (Bergeggi, SV), the order of REE was: Ce>La>Nd>Y>Pr>Gd=Sm>Sc>Dy>Er>Yb>Eu>Tb>Ho>Tm>Lu, while in sites 2 and 3, the order was the same, namely Ce>Y>La>Nd>Sc>Pr>Gd>Sm>Dy>Er>Yb>Eu>Ho>Tb>Tm>Lu, demonstrating that *P. pavonica* samples in these two sites have the same geological “fingerprint”. Moreover, it was evident that these findings reflected a different pattern of REE in seaweeds, not only between the two different marine areas (Malaysia and Mediterranean), but also between the Mediterranean stations that we investigated. Sakamoto and co-authors (2008) investigated REE patterns in seaweed species collected in the Pacific Ocean (Japan). They found that seaweeds accumulated REE at levels 10³ times higher than concentrations detected in seawater, and that the accumulation factor was higher for the heavy REE.

In order to estimate the bio concentration factor (BCF), which is defined as the accumulation of a chemical from water in an organism (Landis et al., 2011), we used the REE concentrations measured in surface waters of the Mediterranean Sea (Censi et al., 2004), ranging from 0.00013 µg L⁻¹ (Yb) to 0.0029 µg L⁻¹ (La). In fact, as REE partitioning is controlled by complexation and binding constants on an ocean-wide basis (Sholkovitz et al., 1994; Strady et al., 2015), we decided to apply them on a regional basin-wide basis, with the approach already utilized in the study by Strady and co-authors (2015).

BCF was usually expressed as the ratio of the concentration of the chemical in the organism and in water; our findings are shown in Figure 6.

The BCFs were expressed in the following decreasing order: Ce>Yb>Pr>La>Nd>Sm>Eu>Tb>Gd>Dy>Ho>Tm>Lu>Er, and with the exception of Yb, the bio concentration factors were higher in LREEs than in HREEs.

258 In a previous investigation in the studied area (Squadrone et al., under review), we found that
259 different macro algae accumulated trace elements from seawater to different extents, and that brown
260 and green macro algae had higher values than red macro algae. In fact, in seaweeds from site 1,
261 important concentrations of iron, aluminum, manganese, copper, nickel and chromium were
262 registered.

263 In this study, the same site (Bergeggi, SV) showed the highest levels of REE.

264 We suggest that REE concentrations in macro algae from sites 2 and 3, being non-contaminated
265 areas, could constitute a baseline record for these elements in Mediterranean seaweeds, due to their
266 characteristic elemental profile. In the presence of anthropogenic sources, such as in site 1, this
267 unique profile was altered, and we can, therefore, suggest the use of REEs as pollution tracers.

268

269 **4. Conclusions**

270 REE, due to their unique chemical properties have become crucially important in many industrial
271 applications, and the global demand is still increasing. Following the consequent release of REE in
272 terrestrial and aquatic environments, due to the extraction process and production of several
273 industrial components, REE can be considered new emerging inorganic contaminants, for which the
274 potential risks for human health and ecosystems have still not been investigated. Seaweeds have
275 been shown to constitute a useful tool for biomonitoring REE, as they can concentrate REE at
276 higher levels than in seawater. This study constitutes the first investigation of REE in seaweeds
277 from the Northwestern Mediterranean Sea, providing the first record, which can be utilized for
278 future comparisons.

279

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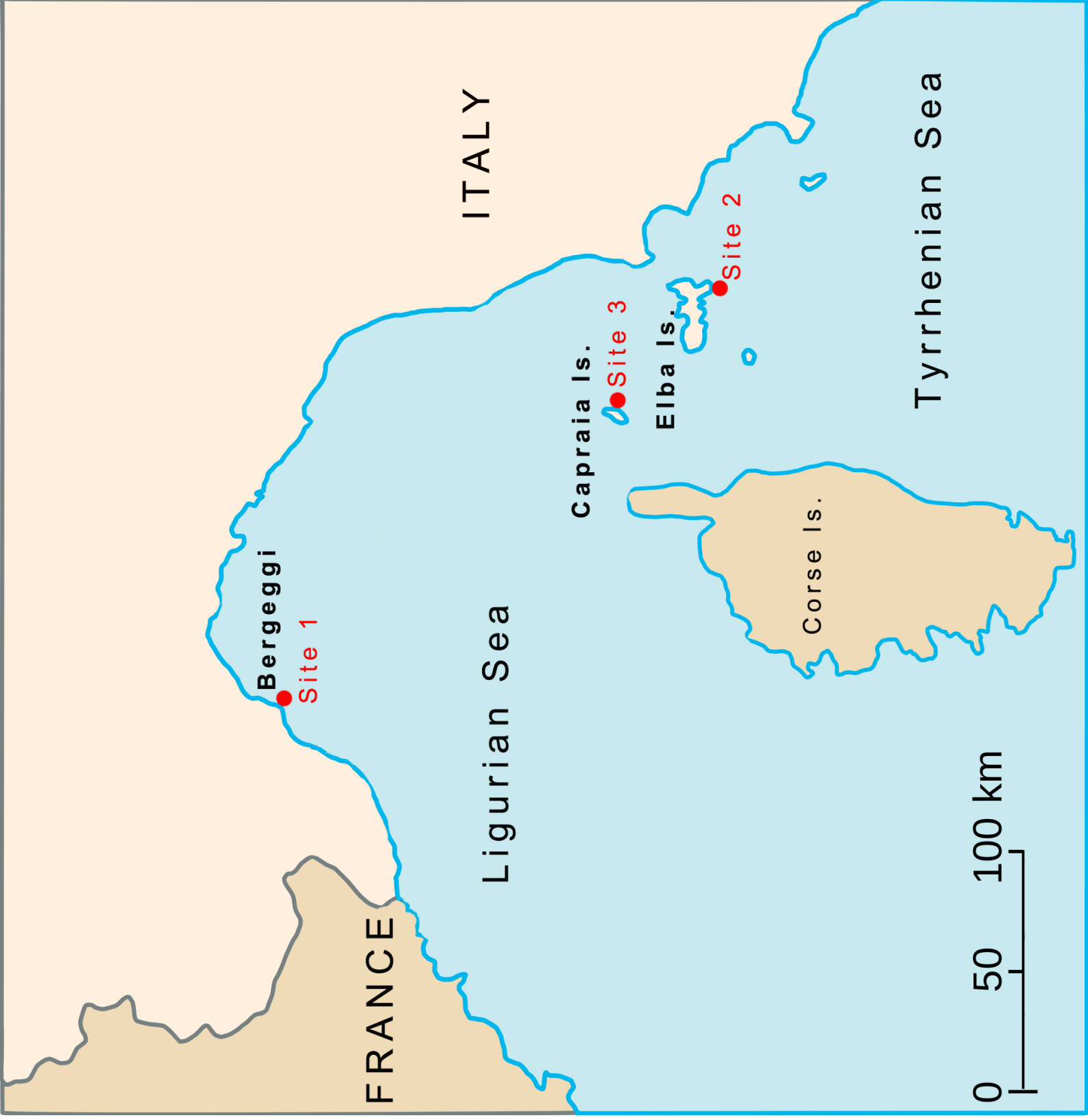
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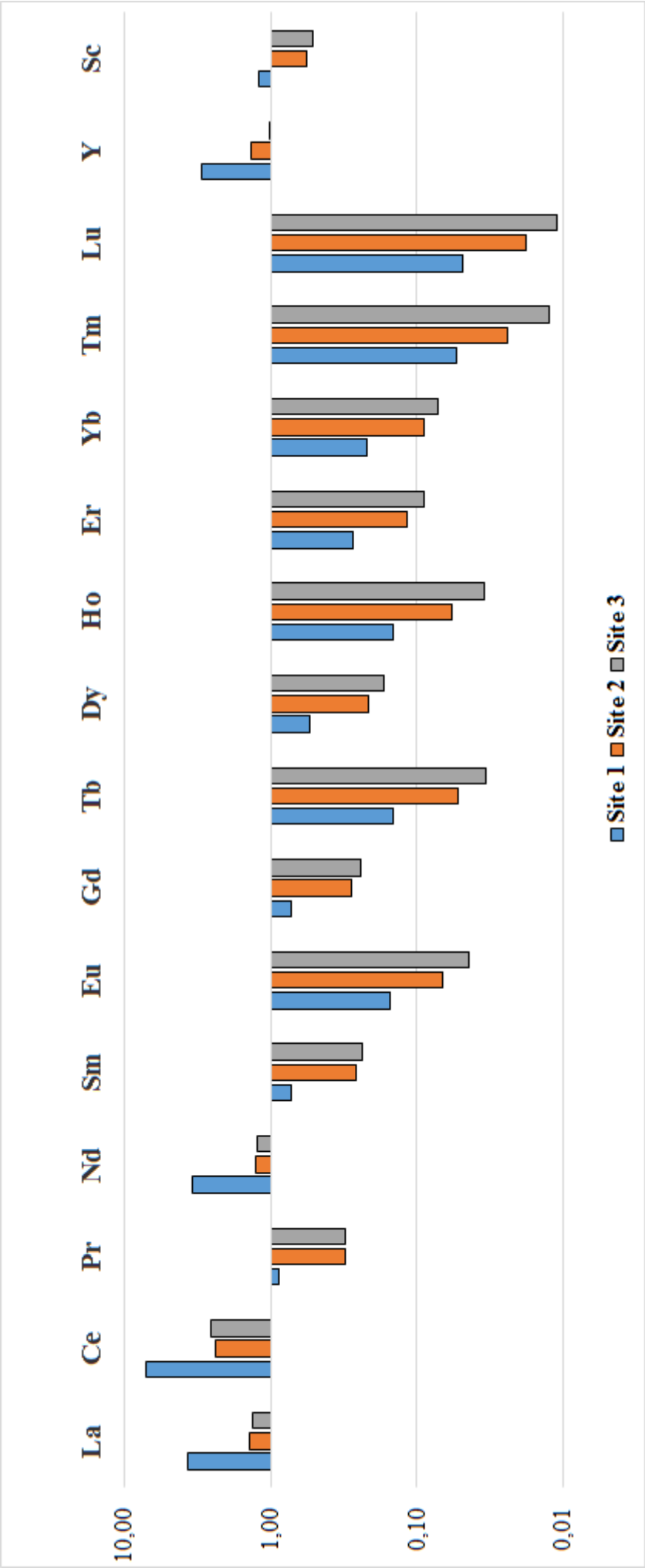
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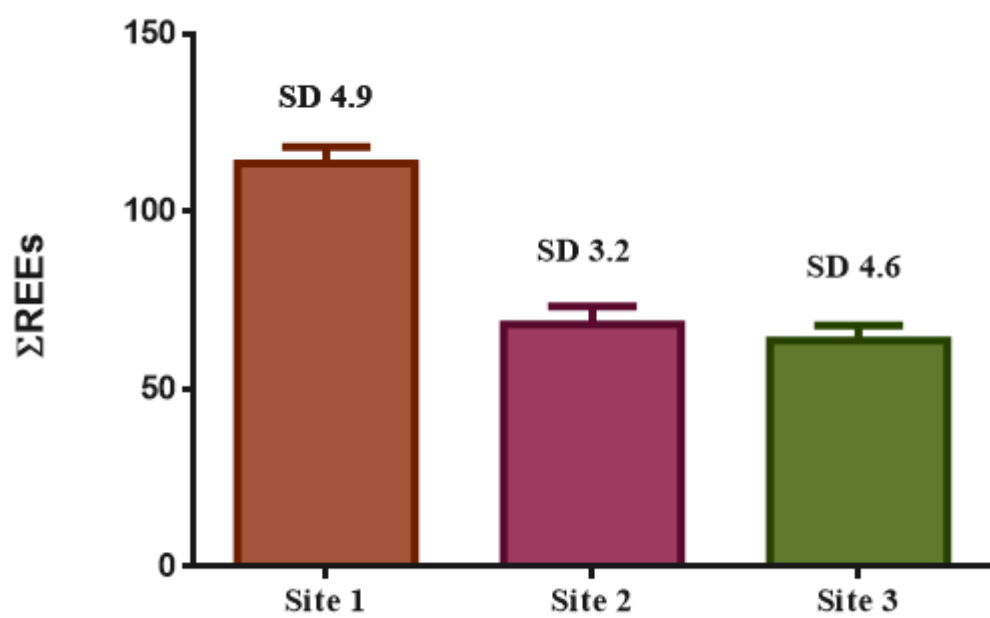
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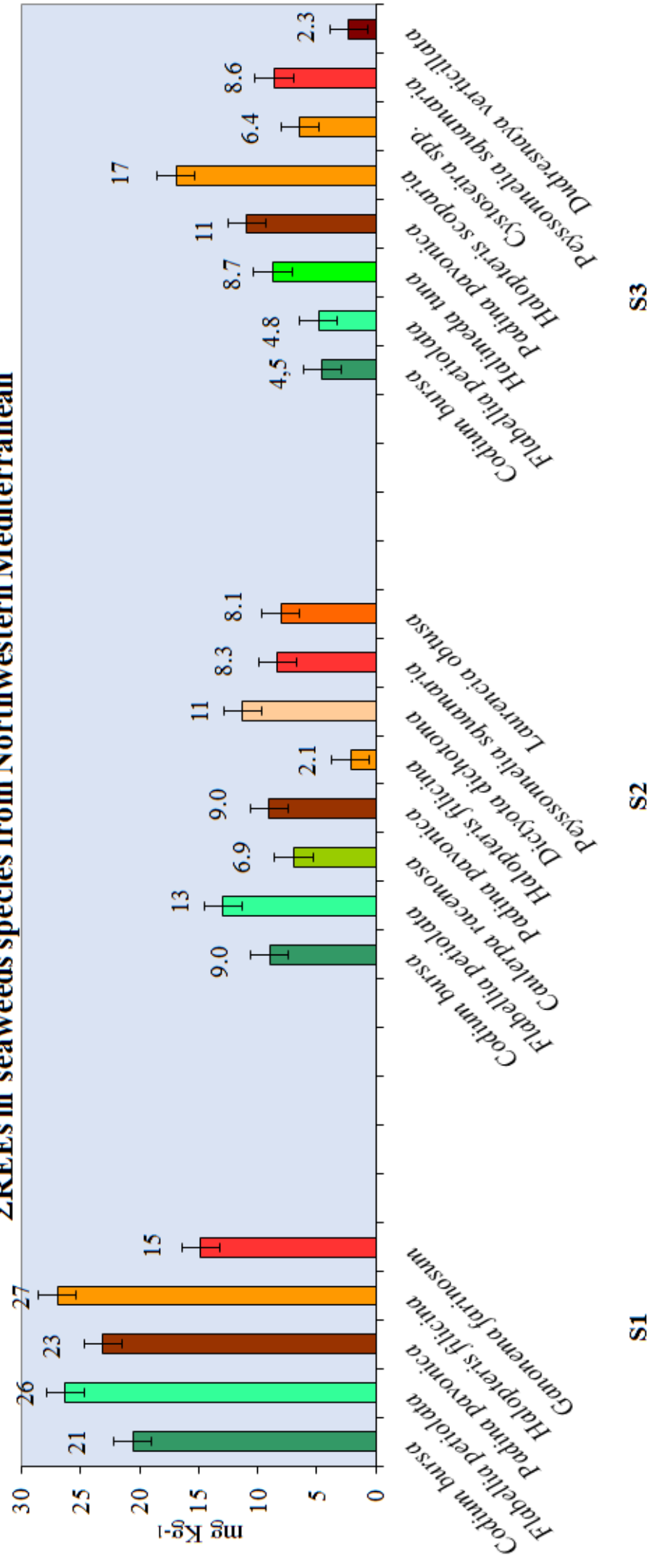
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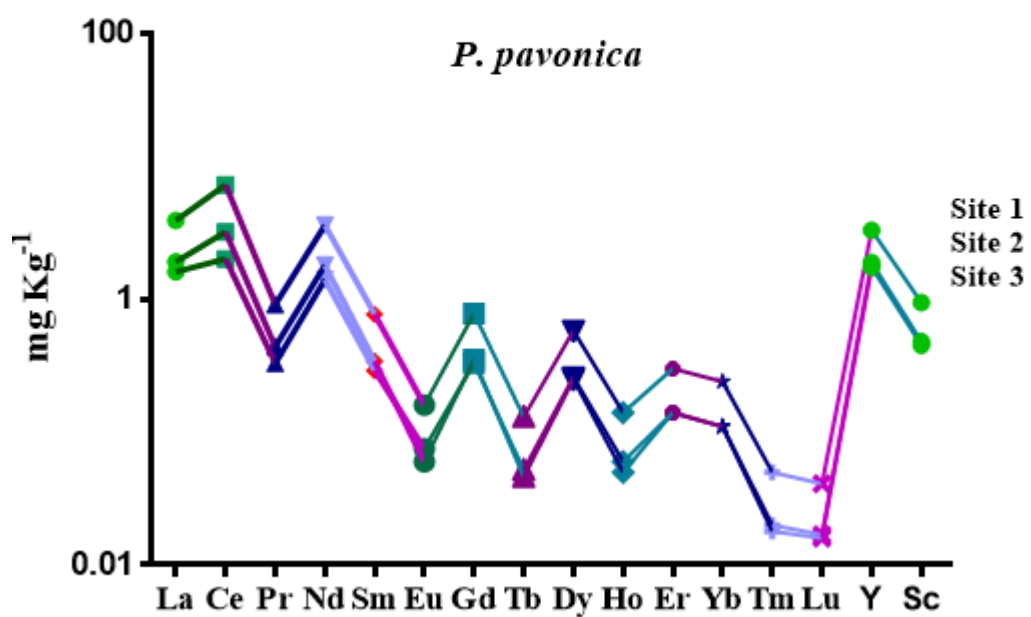
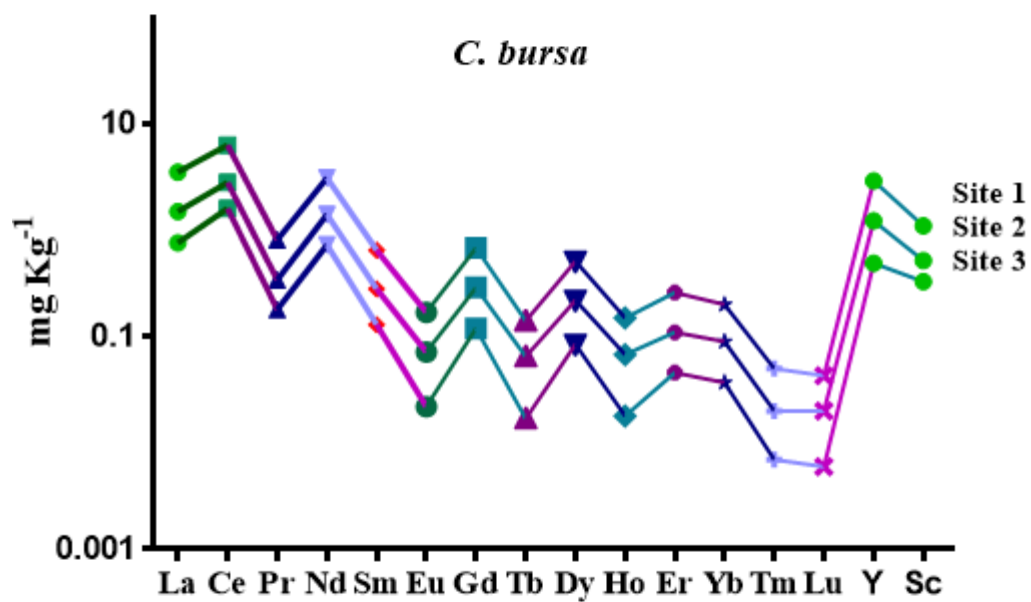
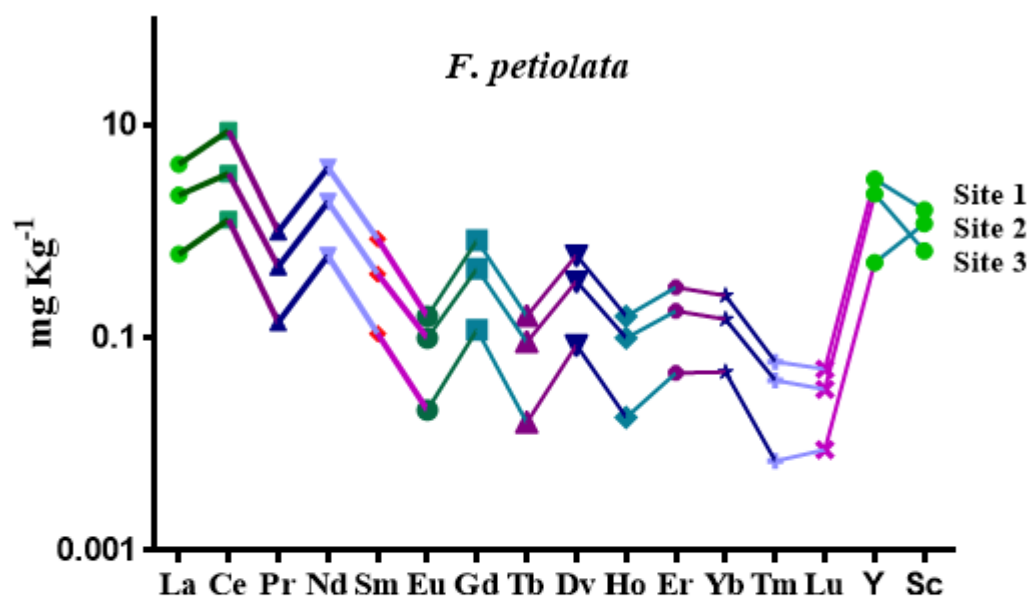


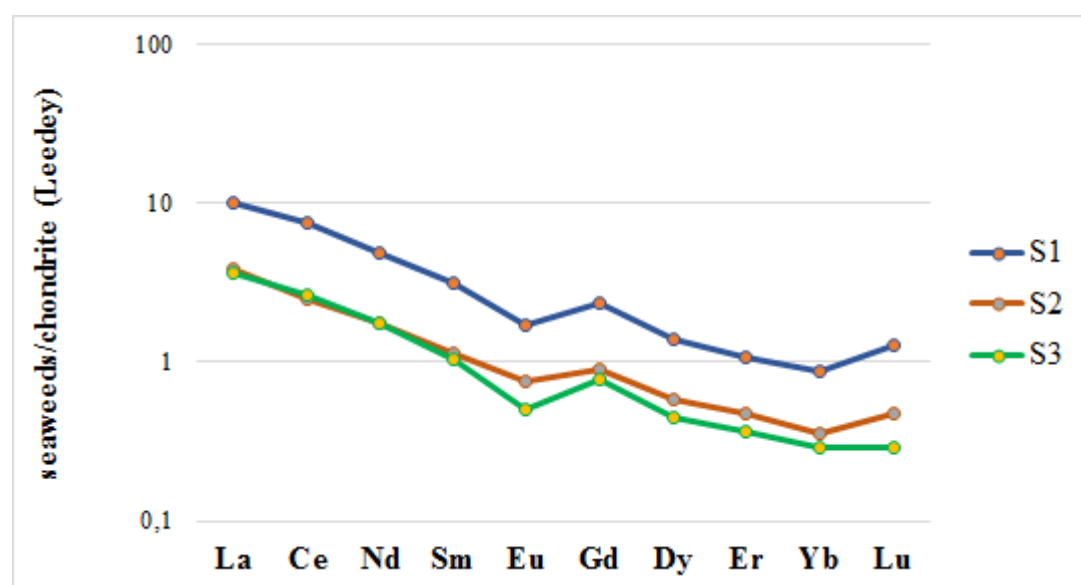


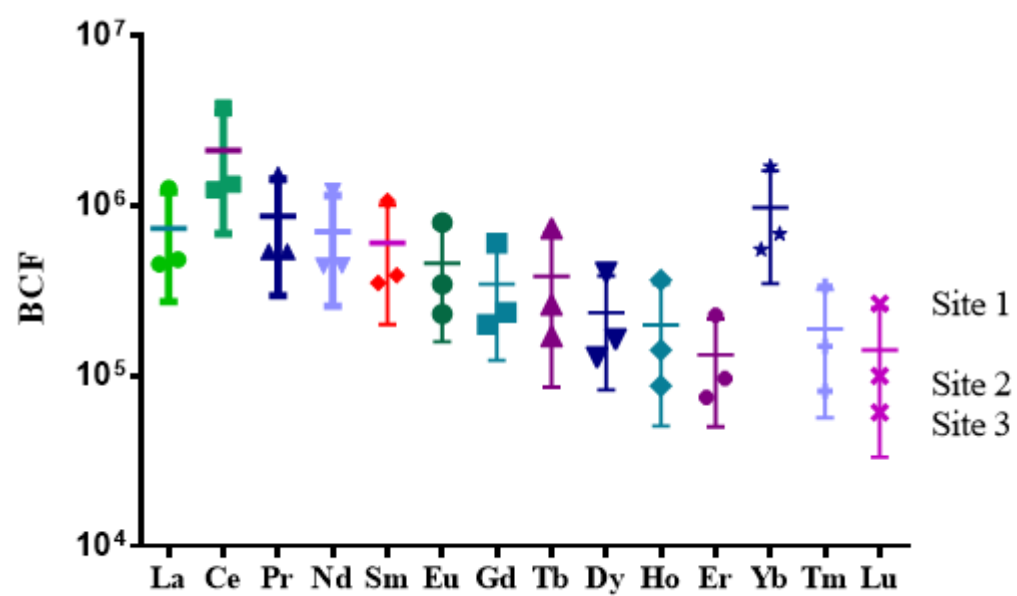


ΣREEs in seaweeds species from Northwestern Mediterranean









Concentrations of REE in macro algae from Mediterranean Sea (mg Kg ⁻¹ d.w.)																				
Site	Species	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Yb	Tm	Lu	Y	Sc	ΣREE	LREE	HREE
S1	<i>Codium bursa</i>	3.5	6.3	0.81	3.1	0.65	0.17	0.68	0.14	0.51	0.15	0.26	0.20	0.050	0.043	2.9	1.1	21	14	5.1
	<i>Flabellia petiolata</i>	4.3	8.8	1.0	4.0	0.85	0.16	0.83	0.16	0.60	0.16	0.30	0.25	0.060	0.051	3.1	1.6	26	19	5.6
	<i>Padina pavonica</i>	3.9	7.2	0.91	3.6	0.77	0.16	0.78	0.13	0.58	0.14	0.30	0.24	0.050	0.041	3.3	0.94	23	16	5.8
	<i>Halopteris filicina</i>	4.3	8.8	1.1	4.1	0.87	0.17	0.87	0.22	0.64	0.22	0.32	0.27	0.080	0.078	3.4	1.53	27	19	6.3
	<i>Ganonema farinosum</i>	2.5	4.8	0.55	2.2	0.46	0.10	0.47	0.08	0.35	0.08	0.19	0.15	0.030	0.030	2.0	0.84	15	10	35
	mean	3.7	7.2	0.87	3.4	0.72	0.15	0.73	0.15	0.53	0.15	0.27	0.22	0.054	0.048	2.9	1.2	22	16	6.5
	SD	0.77	1.72	0.21	0.77	0.17	0.03	0.16	0.051	0.11	0.049	0.051	0.048	0.018	0.018	0.55	0.36	4.9	3.6	1.1
S2		La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Yb	Tm	Lu	Y	Sc	ΣREE	LREE	HREE
	<i>Codium bursa</i>	1.5	2.8	0.34	1.4	0.28	0.072	0.29	0.065	0.22	0.068	0.11	0.090	0.020	0.020	1.22	0.52	9.0	6.3	2.2
	<i>Flabellia petiolata</i>	2.2	3.5	0.47	1.9	0.40	0.10	0.45	0.091	0.34	0.10	0.18	0.15	0.040	0.033	2.26	0.66	13	8.5	3.8
	<i>Caulerpa racemosa</i>	1.1	1.8	0.24	1.0	0.22	0.050	0.24	0.040	0.20	0.050	0.11	0.080	0.020	0.020	1.30	0.50	6.9	4.3	2.1
	<i>Padina pavonica</i>	1.6	2.0	0.33	1.4	0.29	0.075	0.33	0.052	0.26	0.060	0.14	0.11	0.020	0.017	1.88	0.48	9.0	5.6	2.9
	<i>Halopteris filicina</i>	0.29	0.64	0.07	0.31	0.070	0.010	0.070	0.010	0.050	0.010	0.030	0.020	0.031	0.003	0.23	0.25	2.1	1.4	0.5
	<i>Dictyota dichotoma</i>	1.8	3.3	0.41	1.6	0.34	0.090	0.36	0.060	0.27	0.070	0.15	0.11	0.020	0.020	1.61	1.13	11	7.4	2.8
	<i>Peyssonnelia squamaria</i>	1.6	2.6	0.32	1.3	0.25	0.070	0.26	0.050	0.18	0.050	0.090	0.070	0.020	0.010	1.02	0.45	8.3	6.0	1.8
	<i>Laurencia obtusa</i>	1.3	2.3	0.28	1.2	0.25	0.060	0.27	0.050	0.21	0.050	0.11	0.080	0.020	0.020	1.33	0.61	8.1	5.2	2.2
	mean	1.4	2.4	0.31	1.3	0.26	0.066	0.28	0.052	0.22	0.057	0.12	0.089	0.024	0.018	1.4	0.58	8.5	5.6	2.9
	SD	0.56	0.91	0.12	0.47	0.10	0.028	0.11	0.023	0.084	0.025	0.046	0.038	0.008	0.009	0.60	0.26	3.2	2.1	1.0
S3		La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Yb	Tm	Lu	Y	Sc	ΣREE	LREE	HREE
	<i>Codium bursa</i>	0.76	1.6	0.18	0.73	0.13	0.022	0.12	0.017	0.085	0.018	0.046	0.037	0.0070	0.006	0.49	0.33	4.5	3.4	0.9
	<i>Flabellia petiolata</i>	0.61	1.3	0.14	0.59	0.11	0.021	0.12	0.016	0.086	0.018	0.047	0.048	0.0070	0.0089	0.51	1.19	4.8	2.7	0.9
	<i>Halimeda tuna</i>	1.51	3.0	0.37	1.4	0.26	0.040	0.25	0.030	0.17	0.030	0.090	0.071	0.012	0.0090	1.04	0.42	8.7	6.5	1.7
	<i>Padina pavonica</i>	1.9	3.2	0.44	1.8	0.34	0.060	0.35	0.046	0.25	0.050	0.14	0.11	0.018	0.016	1.74	0.45	11	7.7	2.8
	<i>Halopteris scoparia</i>	2.73	6.2	0.65	2.7	0.51	0.10	0.51	0.070	0.34	0.073	0.17	0.13	0.025	0.022	1.87	0.871	17	13	3.3
	<i>Cystoseira spp.</i>	1.00	1.5	0.23	0.99	0.22	0.050	0.25	0.040	0.20	0.040	0.12	0.096	0.016	0.015	1.38	0.32	6.4	3.9	2.2
	<i>Peyssonnelia squamaria</i>	1.52	2.9	0.35	1.4	0.26	0.050	0.26	0.040	0.18	0.040	0.090	0.070	0.013	0.011	1.01	0.40	8.6	6.4	1.8
	<i>Dudresnaya verticillata</i>	0.52	0.80	0.090	0.35	0.060	0.010	0.070	0.010	0.040	0.010	0.020	0.013	0.0020	0.0020	0.20	0.10	2.3	1.8	0.4
	mean	1.32	2.5	0.31	1.2	0.24	0.044	0.24	0.034	0.17	0.035	0.090	0.072	0.013	0.011	1.0	0.51	7.9	5.7	2.3
SD	0.75	1.7	0.18	0.75	0.14	0.03	0.14	0.020	0.10	0.021	0.051	0.039	0.007	0.0062	0.61	0.35	4.6	3.5	1.0	

Table 2 Statistical evaluation

	P value	P value
One-way ANOVA (3 SITES, ΣREE COMPARISON)	P < 0.0001	****
Unpaired t test (SITE 2 AND SITE 3 ΣREE COMPARISON)	P = 0.0811 (P > 0.05)	NS
One-way ANOVA (Site 1, ΣREE interspecies COMPARISON)	P < 0.0001	****
One-way ANOVA (Site 2, ΣREE interspecies COMPARISON)	P < 0.0001	****
One-way ANOVA (Site 3, ΣREE interspecies COMPARISON)	P < 0.0001	****

**** Significant at the 0.01 probability level

NS not statistically significant

Figure 1

Sampling sites, study area.

Figure 2a

Rare earth elements in macro algae from three Northwestern Mediterranean locations (mg Kg⁻¹ dry weight, log scale).

Figure 2b

Box-plot diagrams of Σ REE (mean \pm SD) in the three sampling locations (mg Kg⁻¹ dry weight).

Figure 3

Box-plot diagrams of Σ REE (mean \pm SEM) in the macro algae species (mg Kg⁻¹ dry weight) from the three examined locations.

Figure 4

REE distribution (mg Kg⁻¹ dry weight) in *Flabellia petiolata*, *Codium bursa* and *Padina pavonica* in the three sampling sites.

Figure 5

Chondrite (Leedeey, Oklahoma) normalized patterns of REE in Northwestern Mediterranean macro algae (log scale).

Figure 6

Bioconcentration factors in macro algae from the Northwestern Mediterranean Sea.